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(71) Applicant: **Frediani, Lido**

10093 Collegno (Torino) (IT)

(72) Inventor: **Frediani, Lido**

10093 Collegno (Torino) (IT)

(74) Representative: **Banfi, Paolo**

Bianchetti Bracco Minoja S.r.l.

Via Rossini, 8

20122 Milano (IT)

(54) **Two-layer chrome-plating process**

(57) Disclosed is a galvanic chrome-plating process with a multiple layer of chrome, conducted in an electrolyte bath to which additives able to prevent microcracking of the first layer of chrome are added.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to the use of additives for chrome-plating baths and a process of chrome electrodeposition with the said additives.

STATE OF THE ART

[0002] Chrome-plating, as normally performed, presents numerous drawbacks, the main ones being macrocracks or crazing in the case of deposits thicker than approx. 0.001 mm, which considerably reduce corrosion-resistance; low cathode efficiency; weak penetrating power (in terms of the percentage deviation of the objective distribution ratio of the metal by reference to the theoretical current distribution ratio, as defined by E. Haring and W. Blum); and weak covering power (defined as the minimum current density at which the chrome deposit begins to form); in addition, the internal tensions in the layer deposited reduce the fatigue resistance of the chrome-plated article.

[0003] The various proposed methods of eliminating macrocracks or crazing include high bath temperatures: macrocracks are considerably reduced at the temperature of approx. 70-80°C. However, the use of these high temperatures involves considerable practical difficulties and reduces the hardness of the chrome deposited. The residual tension must be eliminated by heat treatment of the chrome-plated articles at high temperature.

[0004] This invention relates in particular to hard chrome-plating, also known as industrial chrome-plating, which is designed to form chrome deposits that give the underlying metal high corrosion resistance and improved physical and mechanical properties. Its appearance can vary (bright, semi-bright, dull, etc.), as can its hardness, depending on the electrochemical process used. Microcracks may be deliberately introduced for various purposes (e.g. the hydraulic industry, chrome-plating of engine cylinders, etc.) which require lubricant to adhere well to the chrome-plated surface.

[0005] However, sufficient corrosion resistance is still required for these types of chrome deposit.

[0006] Chrome-plating, as normally performed in accordance with known processes, presents two main drawbacks:

- a) deposits thicker than approximately 0.001-0.002 mm are generally subject to cracking or crazing, which considerably reduces their corrosion resistance
- b) the internal tensions in the layer deposited reduce the fatigue resistance of the chrome-plated article.

DESCRIPTION OF INVENTION

[0007] Herein provided is a process for chrome electrodeposition in two layers, wherein the first layer of chrome has a hexagonal crystalline structure, with the result that the deposit is dull, with no cracks, and the second layer is a body-centred cubic lattice and is therefore bright, with microcracks.

[0008] Chrome-plating is widely used to protect metal, especially ferrous articles, against corrosion; there is consequently continual demand for industrial chrome-plating with electrolytic deposits of chrome which offer improved corrosion resistance.

[0009] This invention relates to electro chrome plating processes substantially based on improved chrome-plating baths, with which two or more layers of chrome with different crystalline structures are applied to the article to be chrome-plated using a single galvanic bath.

[0010] As known, a chrome bath obtained with pulsating waves is not cracked, and therefore offers high corrosion resistance. Conversely, its hardness and elasticity (resistance to thermal and mechanical shocks) is lower than that obtained by the conventional method, which means that the use of pulsating waves is not effective for industrial chrome-plating with the mechanical characteristics normally required.

[0011] To eliminate these drawbacks, as the market demands microcracked chrome, this invention uses the two (or more) chrome layer system. A first, non-cracked layer, obtained with the use of an electrolyte solution containing sulphobetaines of heterocyclic bases as additives to inhibit microcracking, is deposited, followed by a second, microcracked layer of chrome with the properties of hardness, elasticity and high protection normally required, because the first, uncracked layer prevents the cracks from reaching the metal base.

[0012] High corrosion resistance results from the choice of the correct thickness of the two layers.

[0013] The process in accordance with the invention is essentially based on the use of specific additives for the galvanic chrome-plating bath. In addition to the sulphobetaines mentioned above, represented by the general formula:

a) $X^+(CH_2)_nSO_3^-$ wherein $n = 1-3$ and X represents a nitrogen containing heterocyclic base selected from pyridine, pyridazine, pyrimidine, pyrazine, piperazine, methyl pyridine, imidazole, nicotinic acid and quinoline,

one or more of the following compounds may be used as additives:

b) heterocyclic bases quaternised with alkane mono- and disulphonic acids of general formula:

b') $CH_3(CH_2)_nSO_3X$, wherein $n = 0-2$ and X is a protonated nitrogen-containing heterocyclic base of the type indicated in paragraph a) above, and

b") $\text{XSO}_3(\text{CH}_2)_n\text{SO}_3\text{X}'$, wherein $n = 1-3$, X and X' are protonated nitrogen-containing heterocyclic bases of the type indicated in paragraph a) above, or hydrogen, provided that at least one of X and X' is a nitrogen-containing heterocyclic base

c) sulphonamides of general formula:

c') $\text{CH}_3(\text{CH}_2)_n\text{SO}_2\text{HN}_2$, wherein $n = \text{integer from } 0 \text{ to } 4$, and

c") $(\text{CH}_2)_n(\text{SO}_2\text{NH}_2)_2$, wherein $n = \text{integer from } 1 \text{ to } 4$.

[0014] The quantity of group a) additives is usually between 0.1 and 2 g/L of solution; the quantity of class b) and c) additives is usually between 1 and 5 g/L. The chrome-plating bath contains 200 to 400 g/L of CrO_3 , preferably 250 g/L, and 2-4 g/L of H_2SO_4 , preferably 3 g/L.

[0015] The electrolytic process can be performed with an average current to the cathode of up to 80 A/dm^2 without any risk of "burning" in the projecting areas with a higher current density.

[0016] The bath temperature is usually between 45 and 60°C .

[0017] In the process in accordance with the invention, a compact layer of chrome with no cracks, with a thickness of approx. 5 microns, is deposited during the first stage, giving the metal beneath it good corrosion resistance. Chrome deposition continues in the same bath with the deposit of a second layer which is substantially microcracked due to the gradual reduction in the inhibitory effect of the additive used, especially the sulphobetaine type, once certain chrome thicknesses are reached. The two-layer chrome-plating thus obtained consequently combines high corrosion resistance with excellent mechanical and lubricant adherence properties.

[0018] At the first stage, which corresponds to the formation of the first layer (or base layer), the method of pulsating-current supply can be used. In this case, a base layer without microcracks can be obtained even with very high thicknesses, thus giving the finished product a very high level of corrosion resistance.

[0019] In known process, after the uncracked base layer of chrome has been applied, additional chrome layers must be applied in a subsequent, different galvanic bath to give the chrome-plated product high corrosion protection (the first layer must obviously be activated to ensure good adherence of the second layer).

[0020] This invention enables the base layer of chrome and one or more successive overlayers to be applied in a single galvanic bath. This enormously simplifies the equipment used and the process compared with the known technique, which requires at least a second chrome-plating bath and a third activating bath.

[0021] Galvanic chrome-plating baths to which alkyl

sulphonic and alkyl polysulphonic acids are added were introduced into industrial practice in the Fifties, and were revived in the Eighties. The aim was to replace the fluorides in the sulphate + fluoride baths used in the known technique, while maintaining the high cathode efficiency of these baths.

[0022] Unfortunately, this proposed alternative to the conventional baths and fluorides was a commercial failure, due to:

- rapid deterioration and consumption of the lead anodes
- degradability of the alkanesulphonic or disulphonic acids into their acid form or their organic salts.

[0023] It has now been found that the use of the additives in accordance with the invention, obtained from nitrogen-containing heterocyclic bases and identified in paragraphs a) and b) above, presents a further advantage, namely that corrosion and encrustation of the lead or lead-alloy anode is much lower than is the case with conventional baths not containing the said compounds.

[0024] Although cathode efficiency is lower than with baths containing known alkanesulphonic acids as additives, the main purpose of this invention is to deposit two layers of chrome in a single operation with a single galvanic bath, strongly reducing lead anode consumption, regardless of cathode efficiency.

Example 1

[0025] Chrome is deposited using an electrolyte solution containing:

- CrO_3 250 g/L
- H_2SO_4 2.5 g/L
- pyridine quaternised with methanedisulphonic acid, 2 g/L
- sulphopropylpyridinium betaine 1 g/L,

[0026] Bath temperature: 58°C , direct current; current density at cathode: 50 A/dm^2 .

[0027] A first, uncracked layer of chrome 5 microns thick is thus formed.

[0028] As chrome electrodeposition continues, a second, microcracked layer (600 microcracks per cm) is formed, making a total thickness of 30 microns.

[0029] The chrome-plating thus obtained has a bright appearance, a hardness of 1000 0.1 HV , and corrosion resistance in saline mist (UNI 5687-73 method) of 125 hours. The corrosion resistance of normal chrome-plating obtained with conventional baths, measured by the same method, is around 40-60 hours, depending on the preparation of the metal base.

Example 2

[0030] In a bath with the composition:

- CrO₃ 250 g/L
- H₂SO₄ 2.5 g/L
- pyridine quaternised with methanedisulphonic acid, 2 g/L
- sulphopropylpyridinium betaine 1 g/L,

bath temperature: 58°C; pulsating current (duration of negative pulse E = approx. 0.3 secs, interval between two negative pulses D = approx. 15 secs); current density at cathode: 50 A/dm².

[0031] A crack-free layer with a thickness of 10 microns is formed.

[0032] Chrome electrodeposition continues with direct current, and a second, microcracked layer (600 microcracks per cm) with a thickness of 20 microns is formed.

[0033] The chrome-plating thus obtained, with a total thickness of 30 microns, has a bright appearance, a hardness of 1000 HV 0.1, and corrosion resistance of 250 hours, measured as stated in Example 1.

Example 3

[0034] In a bath with the composition:

- CrO₃ 250 g/L
- H₂SO₄ 3 g/L
- methanedisulphonamide 2 g/L
- sulphopropylpyridinium betaine 1 g/L,

at the temperature of 58°C, chrome electrodeposition is performed at 20 A/dm².

[0035] A first uncracked chrome deposit with a thickness of 5 microns is thus formed; as chrome electrodeposition continues, and the current density is increased to 45 A/dm², a second deposit of microcracked chrome (600 microcracks per cm) is formed to give a total thickness of 20 microns (5 microns uncracked and 15 microns cracked).

[0036] The chrome-plating thus obtained resembles Example 1 in terms of the characteristics of the chrome deposit.

Example 4

[0037] In a bath with the composition:

- CrO₃ 280 g/L
- H₂SO₄ 3.5 g/L
- pyridine quaternised with methanedisulphonic acid, 3 g/L
- sulphoethylpyridinium betaine 1 g/L,

following the procedure stated in the other examples, the same deposition results are obtained.

Example 5

[0038] In a bath with the composition:

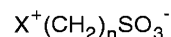
- CrO₃ 300 g/L
- H₂SO₄ 3.5 g/L
- methanedisulphonamide 2 g/L
- N-sulphopropylpyridinium betaine 1 g/L,

the same mechanical characteristics as described in the preceding examples are obtained.

Claims

1. Galvanic chrome-plating process with a multiple layer of chrome, performed in a single electrolytic bath containing 200-400 g/L of CrO₃ and 2-4 g/L of H₂SO₄, maintained at a temperature of 30-80°C, **characterised in that** it comprises the following additives able to prevent microcracking of the first layer of chrome, which has a thickness of up to 5 microns:

a) alkanesulphonic acid derivatives of the sulphobetaine type, represented by the general formula:



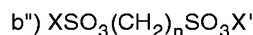
wherein n = 1-8 and X represents a nitrogen-containing heterocyclic base selected from pyridine, pyridazine, pyrimidine, pyrazine, piperazine, methyl pyridine, imidazole, nicotinic acid and quinoline

and at least one of the following compounds:

b) heterocyclic bases quaternised with alkane mono- and disulphonic acids of general formula:

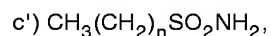


wherein n = 0-2 and X is a protonated nitrogen-containing heterocyclic base of the type indicated in paragraph a) above, and



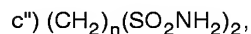
wherein n = 1-3, X and X' are protonated nitrogen-containing heterocyclic bases of the type indicated above, or hydrogen, provided that at least one of X and X' is a nitrogen-containing heterocyclic base

c) sulphonamides of general formula:



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wherein n = integer from 0 to 4



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wherein n = integer from 1 to 4.

2. Process as claimed in claim 1, in which a pulsating-wave current is applied to the electrolytic cell at the first stage, corresponding to the formation of the first, microcrack-free layer. 15
3. Process as claimed in claim 1, in which the sulphobetaine additive is used in amounts of 0.1 to 2 g/L. 20
4. Process as claimed in claim 1, in which the additive comprising a heterocyclic base quaternised with alkane mono- and disulphonic acids is used in amounts of 1 to 5 g/L. 25
5. Process as claimed in claim 1, in which the additive comprising a sulphonamide of alkane mono- and disulphonic acids is used in amounts of 1 to 5 g/L.
6. Process as claimed in claim 1, in which the additives are used simultaneously in the concentrations specified. 30

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EUROPEAN SEARCH REPORT

Application Number
EP 01 12 8826

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	DE 12 43 937 B (SHERING AKTIENGESELLSCHAFT, BERLIN, D) 6 July 1967 (1967-07-06) * examples 1-3 *	1,3	C25D3/10 C25D5/14
A	US 4 450 052 A (MCMULLEN WARREN H ET AL) 22 May 1984 (1984-05-22) * examples 14-16 *	1,3	
A	US 4 006 064 A (NIEDERPRUM HANS ET AL) 1 February 1977 (1977-02-01) * claims 1,2 *	1,4	
A	WO 97 05301 A (STOPPANI LUIGI SPA ; MERELLO GIOVANNI (IT); FREDIANI LIDO (IT)) 13 February 1997 (1997-02-13) * claims 1-4 *	1,5	
A	CH 673 845 A (SOSH AG) 12 April 1990 (1990-04-12) * claims 1,2 * * page 3, line 9-11 * * abstract *	1,5	
A	EP 0 860 519 A (STOPPANI LUIGI SPA) 26 August 1998 (1998-08-26) * abstract * * examples 2,4 *	1,3,4	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	20 March 2002	Haering, C	
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons % : member of the same patent family, corresponding document</p>			

EPO FORM 1503 C3 82 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 12 8826

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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20-03-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 1243937	B		NONE	
US 4450052	A	22-05-1984	AT 31743 T	15-01-1988
			CA 1223546 A1	30-06-1987
			DE 3375166 D1	11-02-1988
			EP 0100133 A1	08-02-1984
			JP 1684201 C	31-07-1992
			JP 3044155 B	05-07-1991
			JP 59028587 A	15-02-1984
US 4006064	A	01-02-1977	DE 2508708 A1	09-09-1976
			BE 838991 A1	27-08-1976
			FR 2302354 A1	24-09-1976
			GB 1529104 A	18-10-1978
			IT 1056193 B	30-01-1982
			JP 1051216 C	26-06-1981
			JP 51110441 A	30-09-1976
			JP 55043512 B	06-11-1980
			NL 7602066 A , B,	31-08-1976
WO 9705301	A	13-02-1997	DE 69601618 D1	08-04-1999
			DE 69601618 T2	11-11-1999
			WO 9705301 A1	13-02-1997
			EP 0783598 A1	16-07-1997
			ES 2131405 T3	16-07-1999
CH 673845	A	12-04-1990	CH 673845 A5	12-04-1990
EP 0860519	A	26-08-1998	AT 200522 T	15-04-2001
			AU 6719398 A	08-09-1998
			BR 9805983 A	31-08-1999
			CN 1246898 T	08-03-2000
			DE 69800697 D1	17-05-2001
			DE 69800697 T2	22-11-2001
			WO 9836108 A1	20-08-1998
			EP 0860519 A1	26-08-1998
			EP 0968324 A1	05-01-2000
			ES 2158672 T3	01-09-2001
			JP 2001511848 T	14-08-2001
			NO 993864 A	11-10-1999
			US 6228244 B1	08-05-2001